

Oxygenates in Water: Critical Information and Research Needs

J. Michael Davis, Ph.D.

Senior Scientist

National Center for Environmental Assessment

U.S. Environmental Protection Agency

Research Triangle Park, North Carolina



Oxygenates in Water: Critical Information and Research Needs

Purposes:

- to identify key issues and information needed to support risk assessment and risk management
- to foster action by serving as a general guide for planning research (but not a detailed research plan)

Process:

ORD-led multi-office Task Group (February 1997)

Internal reviews

Workshop draft (October 1997)

External review draft for public comment (Summer 1998)

Final: December 1998 (www.epa.gov/ncea/oxyneeds.htm)

Principal Authors

J. Michael Davis
(Chair)

National Center for
Environmental
Assessment–RTP

John Brophy
Office of Mobile Sources

Robert Hitzig
Office of Underground
Storage Tanks

Fran Kremer
National Risk Management
Research Laboratory–Cinci.

Michael Osinski
Office of Groundwater and
Drinking Water

James D. Prah
National Health and
Environmental Effects
Research Laboratory

Stephen Schmelling
National Risk Management
Research Laboratory–Ada

Thomas F. Speth
National Risk Management
Research Laboratory–Cinci.

Robert Swank
National Exposure Research
Laboratory–Athens

Anthony N. Tafuri
National Risk Management
Research Laboratory–Edison

Candida West*
National Risk Management
Research Laboratory–Ada

*No longer with EPA

Structure

Background and Needs:

Source characterization

Transport

Transformation

Occurrence

Exposure

Aquatic toxicity

Health effects

Release prevention

Contaminant removal

Appendices:

Physical-chemical properties

List of current projects

Source Characterization

Background

TRI: 1.7 million kg (97% air; <3% surface water)

Mobile source emissions: 40 million kg

LUSTs: 330,000 confirmed leaks since 1988
100,000 estimated future leaks

Relative contributions of point vs. non-point sources
unknown

Needs

- **Determine point and non-point source contributions to oxygenate fluxes to surface and ground waters**
- Model air-land-water fate to predict upper limits of point and non-point source contributions (and other objectives)
- Identify “source signature”

Transport

Background

Oxygenates more water-soluble and less sorbed to soil than BTEX; therefore, may lead or separate from contaminant plume

Models available to predict transport from unsaturated to saturated zone and plume movement in ground water (except for degradation rates)

Modeling indicates MTBE transfers from unsaturated to saturated zone

Needs

- **Biodegradation rates quantified (see Transformation)**
- Field studies to validate models for precipitation infiltration to ground water
- Evaluate deep aquifer vulnerability with fate models
- Field studies to quantify impacts of precipitation, land use, storm-water management on oxygenate loadings to surface/ground waters

Transformation

Background

Data on rates and pathways of MTBE biodegradation are limited, mixed, and inconclusive for surface and ground water

By-products may include TBA and TBF

Natural remediation of ground water contaminated with gasoline may be compromised if MTBE present

Ethanol may inhibit biodegradation of BTEX

Needs

- **Biodegradation rates and pathways measured experimentally under representative geochemical conditions**
- **Identification of degradation by-products and fate**

Occurrence

Background

USGS: 27% of 210 urban wells had 0.2–20,000 µg/L MTBE
(3% >20 µg/L)

MTBE at LUSTs:

- 78% of 236 known LUST sites in Calif.; estimate >10,000 for all Calif. sites
- ~83% of 700 sites in four states (43% of detections >1,000 µg/L)
- 79% of 34 states reported MTBE at >20% LUST sites; 29% reported MTBE at >80% LUST sites

MTBE in drinking water:

- 51% of 49 states had reports of private well contamination; 39% had reports of public well contamination
- 14% of 83 urban d.w. wells had detections; 2% of 949 rural wells; 1 sample >20–40 µg/L
- ~16% of 951 sampled private d.w. wells in Maine had >0.1 µg/L; ~1% had >35 µg/L (projection estimate: 1,400–5,200 wells in state)
- ~16% of 793 Maine public water supplies had >0.1 µg/L; none >35 µg/L
- 2% of 2,120 multiple samples (4% of 450 wells in 16 states) were >0.2 µg/L; max. = 8 µg/L
- <1% of 4,566 d.w. sources in Calif. had >5 µg/L; 0.2% had <35 µg/L

Occurrence (cont'd)

EPA Office of Water:

- 1998 Contaminant Candidate List
- 1999 Unregulated Contaminant Monitoring Rule
- National Contaminant Occurrence Database (if monitoring is required)
- Joint USGS study in Northeast

Standard analytic methods available

Needs

- **Add oxygenates to VOC analyte lists; include transformation products, as appropriate**
- Evaluate sampling and analytic methods
- Analyze databases for trends in water quality/exposures (3–5 yrs from now)

Exposure

Background

Sensory thresholds:

MTBE: 24–135 µg/L (taste); 15–180 µg/L (odor);
even lower thresholds for TAME, ETBE

Population distributions of thresholds have not been
measured

Thresholds and hedonic responses may vary for
individuals and for populations

Cannot presume *avoidance* of exposure

Microenvironmental studies of other VOCs indicate
importance of multi-media, multi-pathway exposures to
“drinking water” (e.g., showering)

Exposure (cont'd)

Needs

- **Statistically representative sampling of water supplies and modeling of multi-media/pathway exposures to estimate population distributions of exposures**
- **Modeling and empirical studies of “high-end” microenvironmental exposure scenarios**
- Statistical sampling to estimate population distributions of sensory thresholds and hedonic ratings

Aquatic Toxicity

Background

Some aquatic toxicity data available for several ether and alcohol oxygenates in selected species

No EPA water quality criteria

Testing underway to fill gaps

Needs

Current actions expected to provide basis for determining whether further work will be necessary

Health Effects

Background

Data on effects of *inhaled* MTBE in laboratory animals and humans, but no data on *ingested* oxygenates in humans (except ethanol)

Limited data on ingested MTBE in animals
(2 acute/subchronic studies; 1 chronic study)

No EPA Health Advisory or RfD for MTBE

Chronic bioassay on TBA in rats and mice

Needs

- **Completion of PBPK modeling and cancer mechanistic studies to allow extrapolation from inhalation data to estimate oral toxicity risk**
- **Subchronic study of MTBE in drinking water (to evaluate toxicity and help validate PBPK model)**
- Conduct health risk assessment of TBA

Release Prevention

Background

Mixed and limited information on effects of oxygenates on gaskets, O-rings, and other materials and components

Although <20%-vol MTBE in gasoline is compatible with elastomers for short term, long-term performance is unknown

Questions have been raised about compatibility of tank liners and effectiveness of leak detection systems

Needs

- **More extensive evaluation of long-term oxygenate effects on tank and pipeline components**

Contaminant Removal

Background

Several methods are available but have not been evaluated for technical feasibility and costs under field conditions; e.g.,

Soil vapor extraction

Low-temperature thermal desorption

Air sparging

Granular activated carbon

Air stripping

Oxidation

Biodegradation

In situ vs. ex situ applications

Needs

- **Evaluate comparative cost-effectiveness of technologies**
- **Optimize best available technologies and develop innovative approaches**

Overarching Needs

- **Perform or update risk characterizations based on above work**
- **Incorporate risk characterizations in risk-risk/risk-benefit comparative analyses**